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RADIOACTIVITIES PRODUCED IN NEUTRON IRRADIATION OF CHLORINE

by

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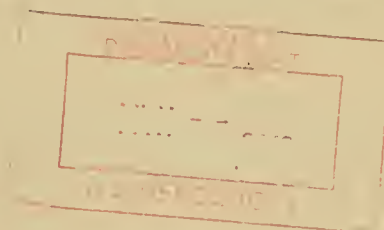
Clinton Laboratories

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Considerable interest has been shown in the use of tracers for the study of a great many chemical reactions. Of the more important elements that have been used for the study of both organic and inorganic chemical reactions, those that can be derived from the bombardment of chlorine have shown themselves to be quite promising. For quite some time cyclotron groups have produced Cl^{38} as a chlorine tracer and S^{35} to be used for following sulfur reactions. However, the short half-life of the chlorine activity has made it quite difficult to work with except at the cyclotron site, and the soft radiation from the sulfur activity has made it difficult to follow. This was particularly true since the chemical procedures used in the past with the sulfur usually have involved the addition of isotopic carrier. It has not been possible to produce large amounts of carrier-free sulfur tracer before the advent of the chain reacting pile.

In conjunction with a program of research related to isotope production, C.P. potassium chloride was placed in the Clinton pile and bombarded for long periods. The samples described in this paper had irradiation times of from 12 to 18 months.

The first activities that were studied were the chlorine activities. Little work was done with the 37 minute activity since its characteristics had been confirmed many times. The other possible activity in the chlorine was Cl^{36}. This had been sought for by O'Neal[1] who set an upper limit of its half-life as about 10^3 years, since he did not find it in a nine months irradiation in a Ra-Be source. The activity was found in minute quantities by Graham and Walke[2], who characterized the beta radiation and gave some evidence for positron and X-ray emission based on a few cloud chamber photographs. They found no appreciable decay in a one year period and postulated that a half-life of the order of 10^3 years was probably correct. They obtained a beta energy of 0.64 Mev.

The procedure for the isolation of the chlorine activities from other radiochemical impurities is given as follows:

To about 0.2 gram of the KCl were added 20 mg of KH_2PO_4 and 20 mg of K_2SO_4 in 5 ml of water. Sufficient $AgNO_3$ was added, according to a standard method, to precipitate the chloride as AgCl. The precipitate was then dissolved in NH_4O after being filtered from the original solution. The hold-back carriers were added again and the silver chloride again precipitated. This cycle was repeated three times. The AgCl was then fused with Na_2CO_3 and the resulting sodium chloride solution distilled from phosphoric acid solution. An aliquot of the chloride was then precipitated with silver nitrate, dried, weighed as AgCl, and counted to determine the specific activity.

The published absorption cross-section of chlorine for slow neutrons is given as 33 barns. The cross-sections of the competing reactions are known to total about 0.7 barns. The cross-section was then assumed to be 32.3 barns for the Cl^{35} $(n,\gamma)Cl^{36}$. Using this value a half-life of 1×10^6 years is found for the long-lived activity. No evidence for decay by other than β^- emission was found.

An absorption curve was taken in aluminum from which we obtained a range as determined by the Feather method of 230 mg/cm^2. This corresponds to an energy of 0.66 Mev. No detectable decay has been noticed during several months. The practical specific activity obtainable in bombarding chlorides in a pile has been issued in the publications of the Isotopes Branch, A. E. C.

Another quite interesting activity produced in the bombardment was the S^{35} from the Cl^{35}(n,p)S^{35} reaction. This has been studied rather extensively by Kamen[3] and Libby and Lee[4]. The irradiation of chlorine containing compounds has already been considered the best way of preparing this activity since it is a slow neutron reaction with a rather high cross-section. Much higher specific activity can be made than in the direct irradiation of sulfur.

Libby and Lee prepared the activity and determined the energy of the beta particle by a specially designed magnetic counter tube which acted in a manner somewhat analogous to a spectrometer. They reported an energy of 0.107 Mev. Kamen has done considerable work on the radiochemistry of sulfur and reports absorption values in aluminum and cellophane which gave an energy of 0.120 Mev. More recently Henriques, et al.[5], have discussed the measurement of the activity with a special electroscope and thin-walled window Geiger counter.

We have separated the activity from chlorine containing compounds with several methods. One of these was done with the aid of added inert carrier and the others yield carrier-free material.

The separation of the sulfur activity from the KCl mentioned in the previous sections was brought about as follows:

To about 0.2 grams of KCl were added 20 mg of K$_2$SO$_4$ in 5 ml of water and 1 ml conc. HNO$_3$. After boiling for a few minutes BaCl$_2$ was used to precipitate the sulfate. The precipitate was centrifuged and washed. The BaSO$_4$ was then mounted on platinum and heated in a Fisher micro combustion furnace at a temperature carefully controlled within 900-950°C. for 1 hour in an atmosphere of hydrogen. The resulting BaS was treated with dilute HCl and the H$_2$S thus formed was passed through lead acetate. The resulting PbS was oxidized with 30% H$_2$O$_2$ to PbSO$_4$. The lead was then metathesized to PbS in a slightly acid solution. The PbS was then centrifuged off and the solution containing the sulfate activity brought back to neutral with a drop of dilute NaOH. This will leave Na$_2$SO$_4$ as the compound containing the activity and a trace of NaCl in the solution. The solution was made up to 25 ml and an aliquot of 0.1 ml was counted. This gave a sample which had a thickness of about 0.1 mg/cm^2. This is a thickness almost negligible for self-absorption corrections but these can be made if desired.

For quantitative measurement of the energy, the most satisfactory method is to obtain carrier-free sulfur activity. The sulfur activity can be extracted most simply in a qualitative manner by the use of ion exchange resins. This method gives a very pure product, with a minimum of effort, but does not allow one to make yield calculations since the chemical yield for the column process is not known.

Carrier-free sulfur has also been prepared by the bombardment of several highly chlorinated hydrocarbons. One of these, on which work has been done, is deca chloro biphenyl

which goes under the trade name of Aroclor 1271. This material was bombarded for a suitable length of time and dissolved in benzene. A small amount of water and a few ml of bromine were added and the solution refluxed overnight. The solid organic compound was then precipitated by the addition of an equal quantity of water and filtered. After distilling off the dioxane- and water from the supernatant solution a small amount of concentrated nitric acid was added to oxidize any organic residue. The activity was taken up in 0.1 N HCl. If desired, the phosphate activity can be precipitated by the addition of phosphate ion and the precipitation of zirconium phosphate or iron phosphate.

Absorption curves can be taken with an ordinary end-window counter and fairly reliable quantitative estimates of the amount of activity present made by extrapolation to zero absorber. In order to determine the quantity present in a given amount of chlorine-containing compound, it was felt that an absolute measure of the yield would be desirable. To do this in terms of millicuries it is, of course, necessary to use a counter rather than an electroscope. Henriques had used a counter with a 2 mg/cm^2 window and had developed an electroscope in which the sample was mounted directly in the chamber of the electroscope. It was felt desirable to have our measurements made on the inside of a counter in a somewhat similar fashion.

To accomplish this end, use was made of a low absorption counter designed by R. L. Butenhoff of our laboratories. In this counter the sample is mounted on a thin Formvar film of about 60 μg/cm^2 thickness. The use of the Formvar is recommended for thin backing of samples to reduce the backscattering. Formvar has been found to be many times stronger than zapon films of the same thickness. The Formvar is also much more resistant to chemical attack than are the zapon films. The absorbers are mounted on a rotating many-sided wheel so that they may be rotated into position between the collecting electrode and the source. The absorbers used here were beaten aluminum which had been calibrated for thickness by alpha counting techniques. The volume of the chamber is about a liter and is of such a size that it can be evacuated and filled in a few minutes.

An aliquot of a larger sample was mounted on the source holder inside the counter and an absorption curve was taken. On this particular instrument are 12 absorbers below 10 mg/cm^2 in thickness. The thinnest absorber is about 0.1 mg/cm^2 which added to the absorption due to the argon gas in the chamber amounting to about 0.6 mg/cm^2. The geometry of the counter was determined by taking a curve on Co^{60} which had been calibrated by use of coincidence measurements made by W. C. Peacock of our Laboratories.

The sulfur source was then counted on a standard counter and an absorption curve taken in the same way that will be done on isotopes released for distribution. The Co^{60} standard was also taken in this way and the geometry thus determined for the standard counter. The curves taken on the two instruments were normalized by using the relative geometry factors as determined by the Co standard and a composite absorption curve drawn. About 20 points were taken on the two machines with 7 points overlapping on the two curves. This composite curve was used then to determine the absolute amount of sulfur activity present and also to determine the energy from the absorption data. From a Feather plot of the absorption data, a range of 35 mg/cm^2 was determined. This corresponds to an energy for the sulfur beta particle of 0.17 Mev.

A very small amount of phosphorous activity was found which had been formed by the

$Cl^{35}(n,\alpha)P^{32}$ reaction on the chlorine. This was separated by the addition of potassium carrier to the solution and the addition of small amounts of potassium sulfate as hold-back carrier. The usual precipitation with magnesia mixture was satisfactory for the separation of the activity from the bulk of the solution after three or four cycles. Additional sulfate hold-back carrier was added after each precipitation. The magnesia mixture had sufficient chloride in it to act as a chlorine activity hold-back. The yield was so small that no great amount of work was done on the reaction except to confirm the half-life of 14.7 days and the energy of 1.7 Mev. as determined by aluminum absorption.
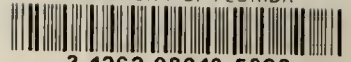
These data are summarized in the following table: (Confirmed values in parentheses).

Reaction	Half-life	Beta Energy (al. Abs.) Mev.
Cl (n, γ)Cl	1 x 106 years	0.66
Cl (n, γ)Cl	(37 minutes)	complex
Cl (n,p) S	(87 days)	0.17
Cl (n, γ) P	(14.7 days)	(1.7)

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(4) Libby and Lee, ibid., 55, 245 (1939)

(5) Henriques, Kistiakowsky, Margnetti, and Schneider, Ind. Eng. Chem., Anal. Ed., 18, 349 (1946)